Pyrolysis of C_6H_6

by

M. B. Colket, III

United Technologies Research Center
Silver Lane, East Hartford, CT 06108

Introduction

Several mechanisms for the pyrolysis of benzene at elevated temperatures have been previously proposed. Unfortunately, none of these mechanisms is entirely satisfactory when both experiments and thermodynamics are considered. Yet, knowledge of benzene decomposition will increase the understanding of the breakup and formation of other aromatic compounds. Consequently, a single-pulse shock tube (SPST) investigation of the pyrolysis of benzene has been performed over the temperature range of 1200 to 2400K. In addition, thermochemical estimates and detailed chemical kinetic modeling have been performed to evaluate the previously proposed mechanisms for benzene pyrolysis.

Description of Facilities and Model

The 3.8 cm (i.d.) single-pulse shock tube (SPST) used in this experiment utilizes the "magic hole" technique for quenching pyrolyzed samples at rates above 10^5K/sec. SPSTs were developed by Glick, Squire, and Hertzberg (1) and the UTRC facility has been described by Colket (2). Gas samples, after dwell times of approximately 700 microseconds, were automatically collected and analyzed for reactant and products using heated gas sampling valves and a Hewlett Packard 5880A gas chromatograph. With a CP Sil 5 CB (from Chrompack, Inc.) capillary column and a silica gel packed column, H_2 and hydrocarbons up to C_{10} were identified and quantitatively analyzed.

Argon (99.999% pure) was obtained from Matheson and LC-grade benzene was obtained from the Burdick and Jackson Laboratory. The initial mixture concentration was 130 ppm benzene in argon and was prepared gravimetrically. Gas chromatographic analysis indicated that impurities included unidentified C_5, C_6 and C_7 hydrocarbons as well as toluene, although the total concentration of impurity was less than 0.2% of the initial benzene.

Detailed chemical kinetics calculations are performed using CHEMKIN(3), LSODE (4), and a version of a shock tube code (5) which has been modified to include the quenching effects in a SPST. Quenching rates varied with shock strength and were calculated using measured pressure traces and assuming isentropic expansion. The modified code also allows monitoring of time-dependent contributions from each reaction to the formation and/or destruction of each species.

Proposed Mechanisms

Mechanisms for the decomposition of benzene are listed in Table I. It is important to note that most are not single-step mechanisms. Radical intermediates equilibrate rapidly and their concentrations are sufficiently low to render them (nearly) undetectable in many systems. Experimental results from the present and previous high temperature works (6,7) suggest that primary stable products are acetylene, diacetylene, and hydrogen and the initial production rate of acetylene is two to three times higher than that of diacetylene. Unfortunately, this information is of minimal use in sorting out the mechanisms since benzene pyrolyzes at high temperatures (relative to pyrolysis temperatures of other hydrocarbons) and all intermediates shown in Table II rapidly pyrolyze to the approximate mixture of acetylene and diacetylene that has been observed.

Mechanism A is the generally accepted reaction sequence; however, only Reaction 1 is understood. The breaking of the C-H bond is believed to be the initiation step in both pyrolytic and some oxidation studies. Its rate has been determined from D-atom production (in pyrolysis of C_6D_6) (8) and from detailed modeling studies of both pyrolysis (9) and oxidation (10). An RRKM fit has been performed by Kiefer, et al (9) using available experimental data and is consistent with thermodynamics. Their k_1^∞ is given by $10^{17.3}$ exp(-118 kcal/RT) sec^{-1}. Knowledge of the mechanism for phenyl decomposition is substantially less than that for Reaction 1. Some information is available on the overall rate, k_3; yet the details of the ring fracturing process have not been defined. The thermochemical estimate by Fujii and Asaba (11) has been until recently the most often quoted rate for this process. More recent modeling (8,9) of benzene pyrolysis has produced similar rates as Ref.11; however, since Reaction 1 is rate limiting over most of the temperatures regimes examined, the modeling results for k_3 are expected to be lower limit estimates with large uncertainties in the temperature dependence. The Fujii and Asaba (11) estimate, $k_3 = 3.16 \times 10^{14}$ exp (-86 kcal/RT) sec^{-1}, was based on an "old" value for the heat of formation for i-C_4H_3 of 102 kcal/mole (12); however, more recent estimates using group additivity (13) and BAC-MP4 (14) techniques fix this value closer to 115 kcal/mole. In addition, n-C_4H_3, which has a ΔH_f of 126 kcal/mole, is the preferred isomer for phenyl decomposition. Consequently, Reaction 3 is over 100 kcal/mole endothermic. If this process involves direct C_2H_2 elimination, then the previous modeling efforts that produced lower limit rates strongly suggest that the high pressure A-factor is at least $10^{17.8}$. This value is orders of magnitude higher than what would be expected for this multibond process. Consequently, it must be assumed that Reaction 3 represents an overall process or that processes involving radicals other than, or in addition to, phenyl are important to benzene decomposition.

One alternative route for benzene decomposition is direct C_2H_2 elimination (Mechanism B) and has received recent support (6,8); however, Kiefer, et al (9) have shown it is not necessary to invoke this step to describe experimental profiles. In addition, it should be noted that the direct elimination is a multibond process which should be unlikely, and presumably involves the intermediate formation of the C_6H_4 diradical. For this intermediate, the effective activation barrier to Reaction 4 may be as high as 180 kcal/mole.

Another possible pyrolysis route involves the production of benzyne, which subsequently decomposes. Unimolecular decomposition of phenyl (Reaction 5) to benzyne is endothermic by 93 kcal/mole, which is nearly as much as Reaction 3. Similar thermochemical arguments can eliminate this decomposition route. The other route, Reaction 6, is a radical termination step and would produce an overall slowing of benzene pyrolysis. Knudsen cell pyrolysis experiments (7) have shown the formation of a C_6H_4 compound. Assuming this compound is benzyne or another product of phenyl decomposition, Smith and Johnson (7) argued that C_6H_4 is an important intermediate during benzene decomposition, especially at elevated temperatures. At least some of the product, however, may be composed of the chained isomers of C_6H_4. These isomers may be produced via hydrogenation of triacetylene, which was also observed in significant concentrations. Consequently, no clear evidence of the importance of Mechanism C is apparent.

Mechanism D appears to be very attractive, since an extrapolation of the rate coefficient (15) for H-atom addition to benzene (Reaction 8) is approximately an order of magnitude higher (Ref. 9) than H-atom abstraction (Reaction 2) at 1600 K. The addition reaction, however, competes with its reverse reaction. Using thermodynamics for $c\text{-}C_6H_7$ derived from measurement of the forward and reverse rates of Reaction 8 (15), Mechanism D can be shown to have a negligible impact on benzene pyrolysis. However, a different set of thermodynamics for $c\text{-}C_6H_7$ reported in Ref. 15 suggests that Mechanism D may play an important role at low temperatures. Detailed modeling calculations using Mechanism D were limited, due to what appears to be rather large uncertainties in both the heat of formation and entropy. Nevertheless, there are attractive features of this decomposition mechanism, especially at low temperatures, and it should be explored further. It is worth noting that Reaction 8 is not sufficiently energetic (only 16 to 26 kcal), that it can be followed immediately by Reaction 9 (71-81 kcal required). Instead, $c\text{-}C_6H_7$ will collisionally thermalize prior to its decomposition to products. Only a minimal acceleration in rate due to the formation of an excited complex can be expected. Further exploration of this route (Mechanism C) should be performed.

With no fully satisfactory alternatives, and the expectation that phenyl must decompose to aliphatics at sufficiently elevated temperatures (when production of phenyl via Reaction 1 is fast), it is prudent to re-examine Mechanism A. One can separate Reaction 3 into the following sequence:

$$C_6H_5 \rightleftharpoons 1\text{-}C_6H_5 \qquad\qquad\qquad 3a$$
$$1\text{-}C_6H_5 \rightarrow n\text{-}C_4H_3 + C_2H_2 \qquad\qquad 3b$$

This sequence is the reverse of the processes suggested for the formation of phenyl during acetylene pyrolysis (17) and has been shown to compare favorably with recent experimental data (2). If one assumes that the ring breaks at the single bond as shown
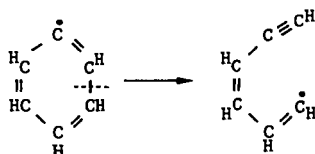
then this is a relatively straightforward process analogous to the decomposition of nC_4H_5; i.e. $CH:CH.CH:CH_2 \rightarrow C_2H_2 + C_2H_3$. Breakage of either of the other two single-bonds would require a more complex process involving H-atom shifting or the formation of energetic intermediates. The resultant linear compound would be expected to decompose to acetylene and $n-C_4H_3$ or re-cyclize to phenyl. Detailed chemical modeling was performed using the reaction sequence in Table II coupled with an acetylenic mechanism similar to that reported (17, 18). A comparison of the model and single-pulse shock tube data is presented in Figure 1 for a series of shocks at an initial concentration of 130 ppm benzene in argon. In this figure, final concentrations produced after a dwell time of 700 microseconds followed by quenching are plotted as a function of initial post-shock temperature. Total pressure for these experiments is approximately seven atmospheres.

The comparison is quite reasonable. The higher fractional decomposition at low temperatures observed in the experiment may be due to impurities from the wall initiating the reaction at low temperature. The residual benzene observed experimentally at elevated temperatures may be caused by sampling a portion of the boundary-layer near the walls of the shock tube. The mechanism proposed in Table II is essentially consistent with Kiefer et al's except that Reaction 3 has been separated to 3a and b. An effective rate constant for Reaction 3 can be estimated by assuming a steady-state concentration for $1-C_6H_5$, i.e.

$$[\ell - C_6H_5]_{s.s.} = \frac{k_{3a}[C_6H_5]}{(k_{-3a} + k_{3b})}$$

therefore k_3 effective $= \dfrac{k_{3a} \, k_{3b}}{k_{-3a} + k_{3b}}$

This curved evalution is depicted as a solid line in Fig. 2 over the temperature regime where sensitivity to this rate was observed. The curve is extrapolated to both low and high temperatures to facilitate comparisons to other evaluations. The relatively high values obtained in this work for k_1 and k_3 effective are not surprising since the rate constant determined in these experiments are expected to be close to the high pressure limiting value.

Conclusions

Previously proposed mechanisms for the pyrolysis of benzene at high temperatures have been reviewed using detailed chemical modeling and a brief thermochemical examination. The most widely accepted sequence, $C_6H_6 \rightarrow C_6H_5 (+H) \rightarrow C_4H_3 + C_2H_2$, is slightly modified to $C_6H_6 \rightarrow C_6H_5 (+H) \rightarrow 1-C_6H_5 \rightarrow n-C_4H_3 + C_2H_2$ and the structure of the linear C_6H_5 intermediate is proposed. Forward and reverse rates are consistent with thermochemistry and experimental data. A benzene decomposition route involving $c-C_6H_7$ and $1-C_6H_7$ was examined, yet sufficiently accurate thermochemistry was not available to reach final conclusions.

References

1. Glick, H. S., Squire, W., and Hertzberg, A., *Fifth Symnposium (International) on Combustion*, p. 393, Reinhold Publishing Corp., New York, 1955.
2. Colket, M. B., To be published in *Proceedings of the Fifteenth International Symposium on Shock Waves and Shock Tubes*, 1986.
3. Kee, R. J., Miller, J. A., Jefferson, T. H., "CHEMKIN: A General Purpose, Problem-Independent, Transportable, Fortran Chemical Kinetics Code Package," Sandia Laboratories, SAND80-8003, March, 1980.
4. Hindmarsh, A. C., "LSODE and LSODI, Two New Initial Value Differential Equation Solvers," ACM SIGNUM Newsletter, 15, No. 4, December 1980.
5. Mitchell, R. E. and Kee, R. J., "A General-Purpose Computer Code for. Predicting Chemical Kinetic Behavior Behind Incident and Reflected Shocks", Sandia National Laboratories, SAND82-8205, March 1982.
6. Kern, R. D., Wu, C. H., Skinner, G. B., Rao, V. S., Kiefer, J. H., Towers, J. A., and Mizerka, L. J., *Twentieth Symposium (International) on Combustion*, The Combustion Institute, p. 789, Pittsburgh, 1984.
7. Smith, R. D. and Johnson, A. L., Combustion and Flame 51, 1 (1983).
8. Rao, V. S. and Skinner, G. B., J.Phys.Chem. 88, 5990 (1984).
9. Kiefer, J. H., Mizerka, L. J., Patel, M. R., and Wei, H. C., J.Phys.Chem. 89, 2013 (1985).
10. Hsu, D. S. Y., Lin, C. Y. and Lin, M. C., *Twentieth Symposium (International) on Combustion*, The Combustion Institute, p. 623, Pittsburgh, 1985
11. Fujii, N. and Asaba, T., *Fourteenth Symposium (International on Combustion*, p. 433, The Combustion Institute, Pittsburgh, 1973.
12. Duff, R. E., and Bauer, S. H., J. Chem. Phys. 36, 1754 (1962).
13. Benson, S. W., *Thermochemical Kinetics, 2nd Ed.*, John Wiley and Sons, New York, 1976.
14. Melius, C., personal communication.
15. Nicovich, J. M. and Ravishankara, A. R., J. Phys. Chem. 88, 2534 (1984).
16. Weissman, M. and Benson, S. W., Int'l. J. Chem. Kin. 16, 307 (1984).
17. Frenklach, M., Clary, D. W., Gardiner, W. C., Jr., and Stein, S., *Twentieth Symposium (International) on Combustion*, p. 887, The Combustion Institute, Pittsburgh, 1985.
18. Kiefer, J. H., Kapsalis, S. A. Al-Alami, M. Z., and Budach, K. A., Combust. Flame 51, 79 (1983).

TABLE I
Previous Mechanisms for
Benzene Pyrolysis

A $\qquad$ $C_6H_6 \rightarrow C_6H_5 + H$ $\qquad$ (1)

$\quad$ H+ $C_6H_6 \rightarrow C_6H_5 + H_2$ $\qquad$ (2)

$\qquad$ $C_6H_5 \rightarrow C_4H_3 + C_2H_2$ $\qquad$ (3)

B $\qquad$ $C_6H_6 \rightarrow C_4H_4 + C_2H_2$ $\qquad$ (4)

C $\qquad$ $C_6H_5 \rightarrow C_6H_4 + H$ $\qquad$ (5)

$\quad$ H+ $C_6H_5 \rightarrow C_6H_4 + H_2$ $\qquad$ (6)

$\qquad$ $C_6H_4 \rightarrow C_4H_2 + C_2H_2$ $\qquad$ (7)

D $\quad$ H+ $C_6H_6 \rightarrow c\text{-}C_6H_7$ $\qquad$ (8)

$\qquad$ $c\text{-}C_6H_7 \rightarrow 1\text{-}C_6H_7$ $\qquad$ (9)

$\qquad$ $1\text{-}C_6H_7 \rightarrow n\text{-}C_4H_5 + C_2H_2$ $\qquad$ (10)

TABLE II
Proposed Reaction Sequence
for Benzene Pyrolysis

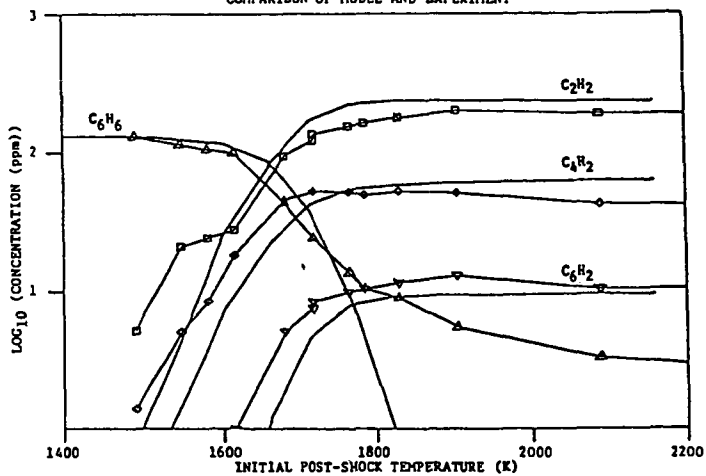|		Forward rate		Reverse Rate		
		$\log_{10}A$	E cal/mole	$\log_{10}A$	n	E cal/mole
1.	$C_6H_6 \rightleftarrows C_6H_5 + H$	16.18	107,900.	10.05	0.98	-5690.
2.	$H + C_6H_6 \rightleftarrows C_6H_5 + H_2$	14.40	16,000.	8.35	1.12	6420.
3a.	$C_6H_5 \rightleftarrows \ell\text{-}C_6H_5$	14.00	65,000.	13.11	-0.68	3300.
3b.	$\ell\text{-}C_6H_5 \rightleftarrows n\text{-}C_4H_3 + C_2H_2$	15.34	38,000.	5.97	1.97	-3610.
11.	$n\text{-}C_4H_3 \rightleftarrows H + C_4H_2$	12.43	37,000.	11.29	0.44	-2790.
12.	$n\text{-}C_4H_3 \rightarrow C_2H + C_2H_2$	14.60	54,000.	7.89	1.66	-3120.
13.	$C_2H + C_6H_6 \rightarrow C_2H_2 + C_6H_5$	13.30	0	12.00	0	12520.

FIGURE 1. 130PPM BENZENE PYROLYSIS
COMPARISON OF MODEL AND EXPERIMENT

FIGURE 2. ARRHENIUS PLOT OF k_3